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(54) Water-in-oil emulsions and their use in paper treatment.

(57) WATER-IN-OIL (W/O) MICROEMULSION CONTAINING AN AQUEOUS SOLUTION OF WATER SOLUBLE ALKALI METAL AND ALKALINE EARTH METAL SALTS, A HYDROPHOBIC SOLVENT AND A SURFACTANT.

SUCH A MICROEMULSION IS USED IN ORDER TO DEACIDIFY PAPERS BY IMPREGNATION.

EP 0 543 372 A1

The present invention relates to microemulsions of water-in-oil (W/O) type and to their use in the treatment of paper products.

More particularly, the present invention relates to W/O microemulsions containing alkali metal and alkaline earth metal salts, and to their use for deacidifying paper and paper products, such as books, drawings, paintings on paper and printings.

Paper is known to undergo degradation over time. The most important factor among those factors which cause paper degradation is the acidity present in paper products.

Such an acidity may have several origins, such as, for example:

- the acidic character or hydrolysis of additives used in paper manufactoring process; and
- the conversion of air pollutants adsorbed by paper (e.g.: SO_2) into strong acids (H_2SO_4);
- lignine degradation;
- oxidation of cellulose and hemicellulose during bleaching, or during the course of natural ageing.

In acidic paper, ageing causes discolouring (yellowing), brittlening, and, in general, loss of mechanical properties of same paper. These effects are more serious if paper contains a large amount of lignine.

The acid-catalysed degradation process of paper products can be stopped by deacidification.

The most widely used deacidification process is based on the precipitation of an alkaline buffer on the cellulosic fibres of paper (W.J. Barrow, Restoration methods; Society of American Archivists, Richmond, Virginia, Oct. 27, 1942). The sheets are soaked in a solution of calcium hydroxide, which neutralizes the acids present; residual calcium hydroxide is subsequently converted into carbonate by means of a bicarbonate solution. Carbonate deposited on paper supplies an alkaline reserve which, during a certain time period, neutralizes the acids coming from same paper and from surrounding environment.

Unfortunately, this process cannot be applied for a bulk treatment of books, because these must be previously disassembled into individual sheets, and the individual sheets must be treated and dried one by one.

Furthermore, the use of such an aqueous solution causes, during the drying, the bonding of pages and the swelling of paper fibres.

The trend in the development of processes for paper deacidification was therefore of depositing sustances which may supply an alkaline buffer, however without using the aqueous vehicle.

GB-A-2 180 248 discloses an expensive process for paper products preservation, in which a polymeric film is coated on paper sheets.

The method disclosed in U.S. patent 4 522 843 uses a suspension constituted by salts of basic metals and a solution composed by an inert halogenated hydrocarbon and a surfactant. Unfortunately, the method requires the use of halogenated hydrocarbons, which are noxious and pollutant.

The process disclosed in U.S. patent 3 676 055 proposes a post-treatment for acidic books. According to this process, the books are first dipped in a solution or suspension composed by alkali metal and alkaline earth metal oxides, and an organic solvent. Subsequently, for the end preservation treatment, a solution of alkyl oxides, or of a mixture of alkyl oxides under pression developed by a propellant (Freon 12) is used.

This process suffers from the following drawbacks:

- two treatment steps;
- ink migration; and
- the use of Freon (i.e., a halogenated hydrocarbon), which causes said process to be an environmentaly incompatible one.

In another process (G. Kelly, Non aqueous deacidification of Books and Paper in Conservation of Library and Archive Materials and the Graphic Arts (G. Petherbridge, ed.), London, Butterworths, 1987, page 117) the dried books are impregnated with diethylzinc vapors at 45°C. Diethylzinc neutralizes the acidity and is converted, when paper absorbs the normal moisture amount, into zinc oxide, thus leaving an alkaline reserve.

Said process requires a very deep pre-drying because the reaction between water and diethilzinc is very fast; this pre-drying operation might cause damages to paper product.

Furthermore, in the presence of oxygen, diethylzinc is explosive, and process safety conditions must be carefully controlled.

Acid paper can be deacidified also in gas phase. Such a process is disclosed in U.S. patent 4 619 735, which uses amines, such as melamine derivatives. Unfortunately, this process makes it possible a low alkaline reserve to be obtained, and furthermore causes paper yellowing and displays toxicity risks.

Therefore, the purpose of the present invention is of overcoming the disadvantages of the processes known from the prior art and of supplying a low-cost product and process for deacidifying paper and paper products in bulk, which process renders such paper products resistant to the effect of acids present in paper and/or deriving from surrounding environment.

The present Applicant has found now that the use of a microemulsion makes it possible an alkaline reserve to be deposited and consequently a protection of paper to be achieved, with a simpple, low-cost and environmentally compatible process, because only surfactants are used, which can be recovered at process end.

"Microemulsion" means a dispersed system of oil-in-water or water-in-oil. "Oil" means a hydrophobic, water immiscible liquid.

These microemulsions are very stable, clear systems. The stability of microemulsions is obtained by using surfactants (and, possibly, co-surfactants) which form a stabilizer monolayer around dispersed water droplets.

The clearness results from dispersed droplets being of small size (50-1500 Å).

The use of a microemulsion of "water-in-oil" (W/O) type as the vehicle for deacidifying substances of paper displays two advantages:

- Owing to the small amount of water contained in the emulsion, it does not cause the fibres to be swollen;
- No problems arise during the drying step, because the dispersent phase is volatile.

Therefore, the subject-matter of the present invention is a microemulsion of water-in-oil type containing the following components:

(a) an aqueous solution of alkali metal and/or alkaline earth metal salts soluble in water in dispersed phase ,

(b) a hydrophobic dispersant agent in continuous phase ,

(c) at least one surfactant agent.

More particularly, the subject-matter of the present invention is a microemulsion of water-in-oil, characterized in that its essential components are the following:

(a) 1-30% by weight of a 10^{-3} - 10 M aqueous solution of water-soluble alkali metal and alkaline earth metal salts,

(b) 50-95% by weight of a hydrophobic organic solvent as the dispersant agent,

(c) 1-40% by weight of at least one non-ionic or ionic surfactant.

When an ionic surfactant is used, the microemulsion possibly comprises from .1 to 20% by weight (based on surfactant) of an organic co-surfactant.

Particularly preferred according to the present invention is a microemulsion containing 5-10% by weight of a 10^{-2} - 10^{-1} M aqueous solution of alkali metal and alkaline earth metal salts, 70-90% by weight of a hydrophobic solvent, 5-25% by weight of a surfactant.

In the microemulsion according to the present invention, water is used in order to act as the vehicle for the alkalifying agent, therefore the amount of water used in the process is really kept at a minimum.

The salts of alkali metals and alkaline earth metals used in the emulsion according to the present invention can be oxides, hydroxides, carbonates and bicarbonates of the metals of Groups I and II, as well as diborates (e.g.: $Na_2B_4O_7$); all of them being water-soluble.

Preferred compound are those containing Mg, Na, Ca; particularly preferred are non-toxicant compounds, such as magnesium ans sodium oxides, carbonates and bicarbonates, and calcium and magnesium hydroxides.

The hydrophobic organic solvent used in the microemulsion according to the present invention has a boiling point comprised within the range of from 0°C to 160°C, preferably comprised within the range of from 50°C to 100°C.

Exemplifying solvents are cyclohexane, n-heptane, n-hexane, isooctane. The preferred solvent is heptane.

The surfactant present in the microemulsion according to the present invention is used in order to stabilize the small dispersed water droplets, reducing the interfacial tension of the system.

Examples of non-ionic surfactants are polyethoxylated long-chain aliphatic alcohols, in particular

$$CH_3-(CH_2)_n-CH_2O-(CH_2CH_2O)_m-CH_2CH_2OH$$

in which n = 1-50, and m = 1-100; the fatty acids monoesters with polyoxyethylene, in particular sorbitol monostearate (monopalmitate, and so forth); ethoxylated nonyl-phenols, in particular

$$CH_3-(CH_2)_8-C_6H_4-O-(CH_2CH_2O)_n-H$$

in which n = 1-100.

Examples of ionic surfactants are AOT (sodium dioctylsulfosuccinate) and SDS (sodium laurylsulfate).

EP 0 543 372 A1

When a non-ionic surfactant is used, the use of only one surfactant is enough. On the contrary, when a ionic surfactant is used, the use is sometimes required of a co-surfactant which decreases the density of surface charge generated by the ionic surfactant, reaching the interface and thus decreasing the interfacial tension. In that way, the co-surfactant makes it possible the dispersion of small water droplets to be achieved. An example of such a co-surfactant is a linear-chain aliphatic alcohol with 3-16 carbon atoms, in particular n-butanol, n-pentanol, n-hexanol.

The microemulsion according to the present invention obtained in that way is suitable for the treatment of acidic paper in order to decrease the acidity thereof, and considerably slow down its degradation over time and alteration of its mechanical properties.

Another object of the present invention is a process for the treatment of paper products, charaterized in that said products are impregnated by dipping into the above disclosed microemulsion, and the surfactant is subsequently removed by washing with solvent and the products are dried.

In the process according to the present invention, the impregnation of paper with the emulsion is carried out at room temperature (25°C). The weight ratio of microemulsion to paper is comprised within the range of from 1:1 to 50:1.

The washing of the impregnated paper is carried out with a solvent, for example with an apolar solvent, such as n-heptane, or an alcohol, such as ethanol.

The resulting treated paper is dried at a temperature comprised within the range of from 0°C to 80°C, preferably comprised within the range of from 25°C to 60°C.

The evaluation of the treatment is carried out by means of measurement of pH value and of alkaline reserve of paper.

According to the preferred process, the W/O microemulsion is prepared by starting from an aqueous solution containing salts of alkali metals or alkaline earth metals, a hydrophobic solvent and a surfactant. The acidic paper is impregnated by being dipped into this microemulsion at room temperature. The ratio of microemulsion to paper, by weight, is comprised within the range of from 2:1 to 20:1.

After the impregnation, paper is washed with the solvent and then is oven dried at the temperature of 50°C. The values obtained for the alkaline reserve and for the pH value of paper demonstrate that the process according to the present invention provides a high de-acidification rate.

Therefore, the process according to the present invention make it possible paper products, such as books (without that they have to be disassembled), drawings, paintings on paper, paintings, documents, and so forth, to be treated in bulk; the fast deposition of alkalifier agents on paper fibres, or fast deacidification of paper; and the removal of soil from paper.

The process according to the present invention is suitable for deacidifying cellulose-based paper, as well as pulp-containing paper.

The process according to the present invention is simple and cheap, because it does not require special equipment, and is environmentally compatible, because the reactants used can be recycled without releasing eco-toxic substances into the environment.

In order to better understand the present invention, and to practice it, some illustrative, non-limitative examples are reported in the following.

The pH value and the reflectance within the blue range [Z (%)] have been determined according to the methods as described by David N.-S. Hon, Historic Textile and Paper Materials II; Chapter 2, page 24, American Chemical Society, 1989.

Example 1

A water-in-oil (W/O) microemulsion was prepared by simply mixing the following components:

77% of heptane,

15% of sodium dioctylsulfosuccinate, and

8% of an aqueous solution of sodium bicarbonate at 5% by weight.

A sheet of pure cellulose Whatman paper with pH 5.7 was immersed in this microemulsion. The paper was soaked for one hour at room temperature (25°C). The ratio of microemulsion to paper, by weight, was 5:1.

So treated paper was sussequently washed with ethanol, and then was dried inside an air-circulation oven at 50°C for 30 minutes.

The following characteristics of paper were determined: pH = 10.0; deposited alkaline reserve 0.10% (as expressed as percent $CaCO_3$ content, based on paper weight).

Example 2

A water – in – oil (W/O) microemulsion was prepared by simply mixing the following components:
80,0% by weight of heptane,
11,5% by weight of sodium dioctylsulfosuccinate, and
8,5% by weight of an aqueous solution of magnesium bicarbonate at 4% by weight.

A sheet of pure cellulose Whatman paper with pH 5.7 was immersed in this microemulsion. The paper was soaked for one hour at room temperature (25 ° C). The ratio of microemulsion to paper, by weight, was 5:1.

So treated paper was subsequently washed with ethanol and then was dried inside an air – circulation oven at 50 ° C for 30 minutes.

The following characteristics of paper were determined: pH = 9.5; deposited alkaline reserve 0.15% (as expressed as percent $CaCO_3$ content, based on paper weight).

Example 3

A water – in – oil (W/O) microemulsion was prepared by simply mixing the following components:
80 % of heptane,
11,5% of sodium dioctylsulfosuccinate, and
8,5% of an aqueous solution of magnesium bicarbonate at 4% by weight.
A pulp – containing paper sheet, visibly yellowed and having a pH value of 5.1, was dipped in this microemulsion. The paper was soaked for one hour at room temperature (25 ° C). The ratio of microemulsion to paper, by weight, was 5:1.

So treated paper was subsequently washed with ethanol and then was dried inside an air – circulation oven at 50 ° C for 30 minutes.

The following characteristics of paper were determined: pH = 8.6; reflectance within the blue range [Z (%)] 57.

The resulting paper was exposed to those conditions which are known to cause an accelerated paper ageing. Therefore, paper was kept stored inside an oven at 90 ° C with a relative humidity of 50%.

Under such conditions, during a one week storage, paper undergoes a degradation rate which corresponds to 147 – 420 years of natural ageing.

The results obtained are reported in following Table 1.

EP 0543372A1 | >

Table 1

Properties	Ageing time, as weeks (Years of natural ageing)									
	0		1 (147-420)		2 (294-480)		3 (441-1260)		4 (688-1685)		5 (735-2100)	
	A	B	A	B	A	B	A	B	A	B	A	B
Z (%)	66	57	49	54	43	53	39	49	38	45	34	44
pH Value	5.1	8.6	4.9	7	4.8	6.7	4.5	6.3	4.7	6.4	4.8	6.3

Z(%) = Reflectance within the blue range;

A = Pristine paper; B = Treated paper

Example 4

A water-in-oil (W/O) microemulsion was prepared by simply mixing the following components: 80 % of heptane,

11,5% of sodium dioctylsulfosuccinate, and
8,5% of an aqueous solution of magnesium hydrogen carbonate at 4% by weight

A book (tied paper sheets having a pH value of 5.1) was dipped into this microemulsion. The book was soaked for one hour at room temperature (25 °C). The ratio of microemulsion to book, by weight, was 2:1.

The so treated book was subsequently washed with ethanol and then was air-dried, at room temperature.

The treated books had a pH value of 7.2.

Example 5

A water-in-oil (W/O) microemulsion was prepared by simply mixing the following components:
67,5% of heptane,
22,5% of LIALET 125/2(R) (a mixture of diethoxylated $C_{12}OH$ and $C_{15}OH$),
10,0% of an aqueous solution of magnesium bicarbonate at 4% by weight.

A sheet of pure cellulose Whatman paper with pH 5.7 was immersed in this microemulsion. The paper was soaked for one hour at room temperature (25 °C). The ratio of microemulsion to paper, by weight, was 5:1.

So treated paper was subsequently washed with ethanol and then was dried inside an air-circulation oven at 50 °C for 30 minutes.

The following characteristics of paper were determined: pH = 9.8; deposited alkaline reserve 0.11% (as expressed as percent $CaCO_3$ content, based on paper weight).

Claims

1. Microemulsion of water-in-oil type, in particular for the treatment of paper products, containing the following components:
   (a) an aqueous solution of alkali metal and/or alkaline earth metal salts soluble in water in dispersed phase ,
   (b) a hydrophobic dispersant agent in continuous phase ,
   (c) at least one surfactant agent.

2. Microemulsion according to claim 1, characterized in that it contains the following components:
   (a) 1-30% by weight of a 10^{-3} - 10 M aqueous solution of water-soluble alkali metal and alkaline earth metal salts,
   (b) 50-95% by weight of a hydrophobic organic solvent as the dispersant agent,
   (c) 1-40% by weight of at least one non-ionic or ionic surfactant.

3. Microemulsion according to any of the preceding claims, characterized in that it preferably contains the following components:
   (a) 5-10% by weight of a 10^{-2} - 10^{-1} M aqueous solution of alkali metal and alkaline earth metal salts;
   (b) 70-90% by weight of an hydrophobic solvent; and
   (c) 5-25% by weight of a surfactant.

4. Microemulsion according to any of the preceding claims, characterized in that said salts of alkali metals and alkaline earth metals used in the emulsion according to the present invention can be oxides, hydroxides, carbonates of the metals of Groups I and II, as well as diborates, all of them being water-soluble.

5. Microemulsion according to claim 4, charaterized in that the preferred salts are magnesium and sodium carbonates and bicarbonates, and calcium and magnesium hydroxides.

6. Microemulsion according to any of the preceding claims, characterized in that the hydrophobic solvent has a boiling point comprised within the range of from 0 °C to 160 °C, preferably comprised within the range of from 50 °C to 100 °C.

7. Microemulsion according to claim 6, characterized in that the preferred solvent is heptane.

8. Microemulsion according to any of the preceding claims, characterized in that said surfactant is of non-ionic type and is selected from poly-ethoxylated long-chain aliphatic alcohols, fatty acids monoesters with polyoxyethilene, ethoxylated nonylphenols.

9. Microemulsion according to claim 1, characterized in that the surfactant is of ionic type and is selected from (C_8 - C_{20}) - alkylsulfates.

10. Microemulsion according to claim 9, characterized in that it comprises a co-surfactant.

11. Microemulsion according to claim 10, characterized in that the co-surfactant is selected from linear chain aliphatic alcohols with 3-16 carbon atoms.

12. Process for the treatment of papers and paper products, in particular for deacidifying them, characterized in that it comprises the following steps:
- -- impregnating the paper product by dipping said paper product in a microemulsion of water-in-oil type containing an aqueous solution of water soluble alkali metals and/or alkaline earth metal salts, a hydrophobic dispersant agent and a surfactant agent,
- -- removing said surfactant agent from said paper product by washing with solvent, and
- -- removing said solvent from said paper product by evaporation.

13. Process according to claim 12, characterized in that the ratio of microemulsion to paper, by weight, is comprised within the range of from 1:1 to 50:1.

14. Process according to claim 13, characterized in that the ratio of microemulsion to paper, by weight, is preferably comprised within the range of from 2:1 to 20:1.

15. Process according to any of claims from 12 to 14, characterized in that the washing solvent is an apolar solvent, preferably n-heptane.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 11 9718

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	FR-A-2 578 198 (KOPPERS COMPANY, INC.) * the whole document *	1,4,5	D21H25/18
A	US-A-3 898 356 (WILLIAMS ET AL.) * the whole document *	12-15	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	02 FEBRUARY 1993	SONGY Odile

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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E : earlier patent document, but published on, or after the filing date
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